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UTILIZATION OF AN ACCELERATING RATE CALORIMETER FOR THE THERMAL DECOMPOSITION STUDIES OF AMMONIUM NITRATE AND AMMONIUM NITRATE - FUEL OIL EXPLOSIVES

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Canadian Explosives Research Laboratory

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by

P. Lee* and R.R. Vandebeek**

ABSTRACT

An accelerating rate calorimeter (ARC) was used to investigate the thermal decomposition of six types of ammonium nitrate (AN) and ammonium nitrate - fuel oil (ANFO) samples. The phase transitions of AN and some modifications of the system for future tests were also discussed briefly.

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L'USAGE D'UN CALORIMÈTRE À RÉGIME ACCÉLÉRÉ POUR ÉVALUER LA
DÉCOMPOSITION THERMIQUE D'ÉCHANTILLONS DE NITRATE D'AMMONIUM
ET DE MÉLANGES EXPLOSIFS AU NITRATE D'AMMONIUM ET AU FUEL OIL

par

P. Lee* et R.R. Vandebeek**

RÉSUMÉ

Il s'agit de l'usage d'un calorimètre à régime accéléré (CRA) pour évaluer la décomposition thermique de six sortes d'échantillons de nitrate d'ammonium et de nitrate d'ammonium - fuel oil (ANFO). On discute aussi brièvement des phases de transition du nitrate d'ammonium et des modifications à apporter au système en vue de futurs essais.

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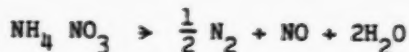
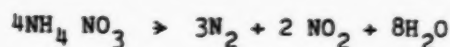
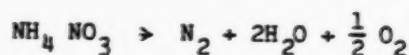
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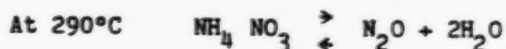
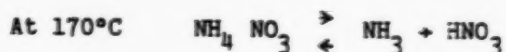
INTRODUCTION

Ammonium nitrate is one of the most widely used components of explosives due to its appreciable chemical stability and low sensitivity to friction and to shock. The thermal behaviour, including both phase transitions (1-4) and thermal decomposition of ammonium nitrate has been extensively studied. Ammonium nitrate is a relatively stable compound which first decomposes and then explodes if heated while confined (5,6).

Pure ammonium nitrate starts to decompose at its melting point of 169.6°C. Complete detonation and incomplete explosion are defined by the following equations (7).



However, Feick and Hainer (7) suggest the following equations for ammonium nitrate's thermal decompositions.



The complete anhydrous salt does not decompose until 300°C but sublimates. Different studies suggest various paths of decomposition. None of the reactions occur as a single reaction, but is always accompanied by others (8). A number of researchers also investigated the influence of other compounds on the thermal decomposition of AN (9-11).

An accelerating rate calorimeter (ARC) is used to examine the thermal stability of different types of ammonium nitrate (AN) and ammonium nitrate - fuel oil (ANFO) explosives. Since details of design, operation and performance of ARC have been published elsewhere (13-17), the description of the instrument will not be discussed in detail.

EXPERIMENTAL

All measurements were conducted in wide-mouth cylindrical Hastelloy C bombs weighing approximately 49 g each. Six stainless steel screws secured a thin nickel disk and a Teflon gasket to a flange on the bomb.

The weight of the sample was determined by the effect of thermal inertia, ϕ , as discussed in the literatures. A series of tests consisting of varying the sample weight so as to vary the ϕ were done. A 1.5 g sample corresponding to a ϕ of 9 was used as it did not cause major damage to the calorimeter. The ϕ chosen had a numerical value close to the ideal situation at which ϕ was equal to 1.

The bomb temperature was monitored by a thermocouple (type N) which was attached to the outside of the bomb and referenced to an ice point. The step heat method was used to study the phase transitions and exothermic decomposition of different types of AN and ANFO explosives. The first step was to enter "heat" mode to heat the sample and container to the start temperature. Then the calorimeter entered "wait" mode and it was allowed to thermally stabilize for 30 min. Next came "search" mode where the self-heat rate was monitored at a threshold detection limit, usually 0.02°C/min. The process of "heat-wait-search" was continued until a self-heat rate greater than 0.02°C/min was detected. After detection of the exotherm, time, temperature, heat rate and pressure were monitored until the end of the reaction.

Isothermal age method was also employed to study the stability of AN and ANFO samples. Basically, the sample was maintained adiabatically at a given temperature for a certain period of time. If a self-heat rate greater than 0.02°C/min was detected during the aging, the system automatically went into the data acquisition mode until the thermal runaway was complete. If the sample survived the aging time without exotherm, then the sample was step heated to generate the self-heat curve.

Samples consisted of the following:

1. Ammonium nitrate granular, Anachemia Chemicals Ltd.
2. Ammonium nitrate aeroprills (34-0-0), ammonium nitrate fertilizer.
3. Ammonium nitrate aeroprills - dodecane (B.P. 216.3°C) (94:6).

Sample 3 was a laboratory prepared mixture. Based on the analysis of oil content of the coated aeroprills, it was found that the oil coating was evenly distributed.

4. ANFO, Nilite FR, DuPont.
5. Ammonium nitrate - C prills, C.I.L.
6. ANFO, AMEX II, C.I.L.

No detailed thermal history could be obtained for the samples with samples 5 and 6 being recently manufactured by the company. All the samples were conditioned at room temperature before they were used in the ARC tests.

RESULTS AND DISCUSSION

I. Phase Transitions of Ammonium Nitrate

Ammonium nitrate is hygroscopic and crystallizes in five different polymorphic forms. It was studied by other investigators (3,7,12) and the results are summarized in Table 1.

Table 1 - Literature values of crystalline transformations of ammonium nitrate

Crystalline form	Stable temperature range	Transition temperature
Phase I	125°C to 169°C	+169.6°C
Phase II	84°C to 125°C	+125.2°C
Phase III	32°C to 84°C	+ 84.2°C
Phase IV	-16°C to 32°C	+ 32.1°C
Phase V	below -16°C	- 18°C

Although the ARC was originally designed for exothermic reaction studies, the endothermic phase transitions could also be detected during the step heat cycle. When an endothermic reaction occurred, the digital printed data showed a high negative self-heat rate and it took a longer time to heat up than a normal step. The above phenomena were also demonstrated at the strip chart recorder. However, the ARC does not give the accurate temperature for the endothermic reaction as the DSC result.

AN was step heated using 2°C steps from 24°C to 172°C and checked for endothermic transitions. In the cooling cycle, AN was cooled automatically beginning with the end temperature. The temperature and cooling rate were monitored at 30 min intervals and were plotted manually. The reverse phase transitions were indicated at the strip chart. Experimental data is presented in Table 2 and shows endothermic phase transitions at 40°-42°C, 84°-86°C, 124°-126°C and 168°-170°C. When AN was cooled, phase (II) changed directly to phase (IV) at 48°-49°C whereas the transitions at 32°C and 84°C were not observed. Figure 1 indicates the reverse phase changes during the cooling cycle which influenced the cooling rate. The fusion temperature and the 125°C temperature inflections were consistent through all the step heat experiments. The behaviour of AN at 32°C and 84°C appeared to be irregular and AN aeroprills did not show the endothermic transition at 40°C as AN granular. The reason for the occurrence of the short exotherm at 50°C for AN aeroprills was unknown.

II. Thermal Decomposition of Ammonium Nitrate (AN) and Ammonium Nitrate - Fuel Oil (ANFO) Explosives

A. Step heat studies

The step heat logic was employed in the thermal decomposition studies for six types of AN and ANFO samples. After equilibration at 50°C or 100°C, an iterative "5°C heat - 30 min. wait - search" sequence was conducted until the appearance of a heat rate greater than 0.02°C/min. After detection of an exotherm, time, temperature and temperature rate were monitored continuously until the end of the reaction. Sample size was 1.5 g giving a Ø of 9. The Hastelloy C bomb used was only sealed with a Teflon disk for the experiments on the AN granular samples.

Table 2 - ARC data of phase transitions of AN

Run No.	Sample	ϕ	Heating cycle			Cooling cycle	
			Endothermic temperature (°C)	Step heat time (min)	Temp rate (°C/min)	Transition temperature (°C)	
87	AN granular	3.8	40-42 (IV) $\rightarrow$ (III)	9	-0.245	48-49	
			84-86 (III) $\rightarrow$ (II)	11	-0.013	-	
			124-126 (II) $\rightarrow$ (I)	13	-0.034	122-123	
			167-170 (I) $\rightarrow$ liquid	24	-0.002	163-164	
94	AN granular	3.4	38-40	13	-0.048	48-49	
			86-88	11	-0.043	-	
			126-128	17	-0.029	121-124	
			168-170	17	-0.024	163-165	
111	AN aeroprills	3.4	50	5	exotherm 0.138°C/min	47-49	
			84-86	10	-0.014	-	
			126-128	26	-0.037	121-123	
			168-170	40	-0.010	165-166	
113	AN aeroprills +1% H ₂ O	3.4	50	6	exotherm 0.292°C/min	48-49	
			84-86	7	-0.008	-	
			124-126	28	-0.022	122-123	
			154-156	13	-0.005	154-155	

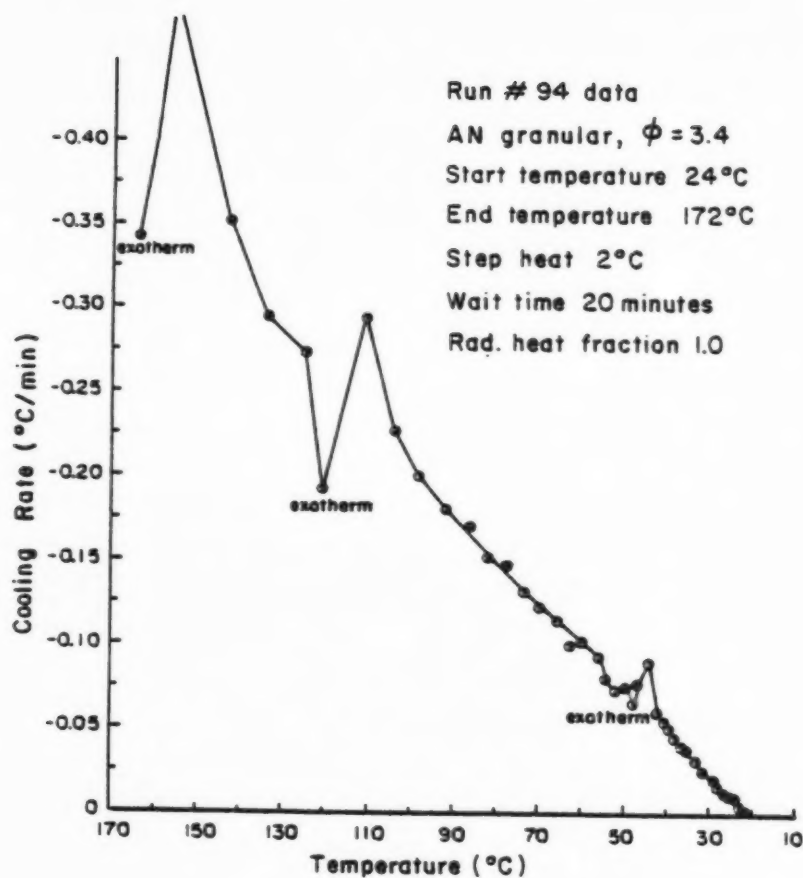


Fig. 1 - Phase transitions of ammonium nitrate obtained on cooling.

When the AN samples were step heated, the endothermic phase transitions were always detected at 125°-130°C and 165°-170°C steps. The short exotherms occurred in the range of 190°C to 210°C which indicated that decomposition occurred after the melting point of AN. They showed a similar trend of fluctuation before the major exothermic reaction which lead to ignition. The initial temperature of the major exotherm was determined at above 210°C. However, the initial time for the exotherm was not reproducible due to the fluctuation of the short exotherms. Pressure rise was indicated at the sealing disks but unfortunately it could not be measured by the transducer due to the blockage and corrosion problems of the molten AN to the connecting tubing. Table 3 presents the results of the decomposition of AN and ANFO. Figure 2 shows the self-heat rate vs temperature plot of the decomposition of AN. The self-heat rate at ignition was faster than 100°C/min and it could not be traced accurately by the instrument.

Figure 3 shows the temperature and self-heat rate vs time plots of four different samples. The AN granular, AN aeroprills and AN aeroprills-dodecane mixture indicated similar thermal decomposition profiles. The self-heat rate increased very rapidly after 2°C/min and it determined the temperature before ignition. The ignition characteristic of commercial ANFO was fast and vigorous. For example, the self-heat rate increased drastically from 0.3°C/min to over 100°C/min in 0.02 min. After ignition, the weight loss of the samples ranged from 98% to 99% with brown residue which was insoluble in water.

Even though the Hastelloy C cylindrical bomb could be used to solve the loading difficulty of solid materials, it still had the problem of splashing of molten material and residues to the calorimeter. The corrosive material caused some damage to the calorimeter and the radiant heater.

B. Isothermal age studies

The step heat method indicated that the AN samples were stable to 200°C, therefore the temperatures for isothermal age tests were chosen in that range. Hastelloy C cylindrical bombs with metal and Teflon sealing disks were used. Sample size was 1.5 g giving a ϕ of 9. After the isothermal aging period, the sample was step heated 5°C to generate the self-heat curve. The isothermal study data is summarized in Table 4.

Table 3 - ARC results on AN and ANFO decomposition

1st exotherm										
Run No.	g	Start temp	but stop	Initial			Before ignition			ΔT_{AB} (°C)
		(°C)	(°C)	T_0 (°C)	M_0 (°C/min)	t_0 (min)	T (°C)	M (°C/min)	$t_0 + t$ (min)	
<u>AN granular</u>										
80	47.9	50	-	231.19	0.041	761.69	240.37	2.500	54.82	11.27
81	25.0	50	-	216.00	0.033	1262.52	232.09	2.190	105.97	38.72
83	19.0	100	197.08	204.21	0.034	893.35	233.71	2.050	370.79	66.96
84	11.5	100	180.80	191.95	0.032	741.40	228.62	2.172	474.84	70.46
85	9.0	100	190.90	197.42	0.023	829.64	231.63	2.000	525.47	78.50
86	7.0	100	191.03	204.10	0.030	920.84	230.28	2.032	368.82	72.56
99	9.0	100	196.01	218.82	0.033	1161.76	260.89	2.157	368.43	72.29
<u>AN aeroprills</u>										
93	9.2	50	195.99	210.36	0.022	1372.56	246.95	2.050	353.91	73.28
92	9.2	100	206.04	214.23	0.044	341.72	251.37	2.068	218.73	67.77
95	9.0	100	201.07	215.59	0.028	1013.43	259.63	2.000	585.63	78.39
124	9.2	100	206.03	212.39	0.025	962.51	255.91	2.000	635.74	77.72
<u>AN aeroprills - dodecane (94:6)</u>										
114	13.0	50	170.96	204.78	0.019	1500.30	245.86	2.050	718.34	71.40
115	9.1	50	-	221.12	0.033	1343.95	241.21	2.000	133.54	61.04
116	9.0	50	200.99	229.74	0.026	1862.39	263.32	2.000	307.25	66.55
118	9.2	50	216.21	224.98	0.043	1444.88	261.00	2.000	208.96	73.10
125	9.0	100	211.09	233.15	0.024	1255.98	266.81	2.032	229.41	68.80
126	9.2	100	211.11	217.45	0.024	987.59	255.48	2.105	389.92	74.03
<u>AN-C prills, C.I.L.</u>										
130	9.2	100	201.14	225.20	0.039	1282.12	262.74	1.904	251.82	68.11
134	9.0	100	196.21	218.61	0.031	1136.74	262.70	2.000	355.85	77.39
<u>ANFO, Nilite FR, DuPont</u>										
128	9.2	100	191.09	234.54	0.028	1317.62	244.35	0.561	161.27	20.51
129	9.0	100	201.13	238.34	0.044	1248.60	252.42	1.952	165.36	28.73
<u>ANFO, AMEX II, C.I.L.</u>										
131	9.0	100	196.10	228.18 (ignited during step heat)						-
133	9.2	100	186.09	229.05	0.071	1668.56	235.00	0.344	51.35	-

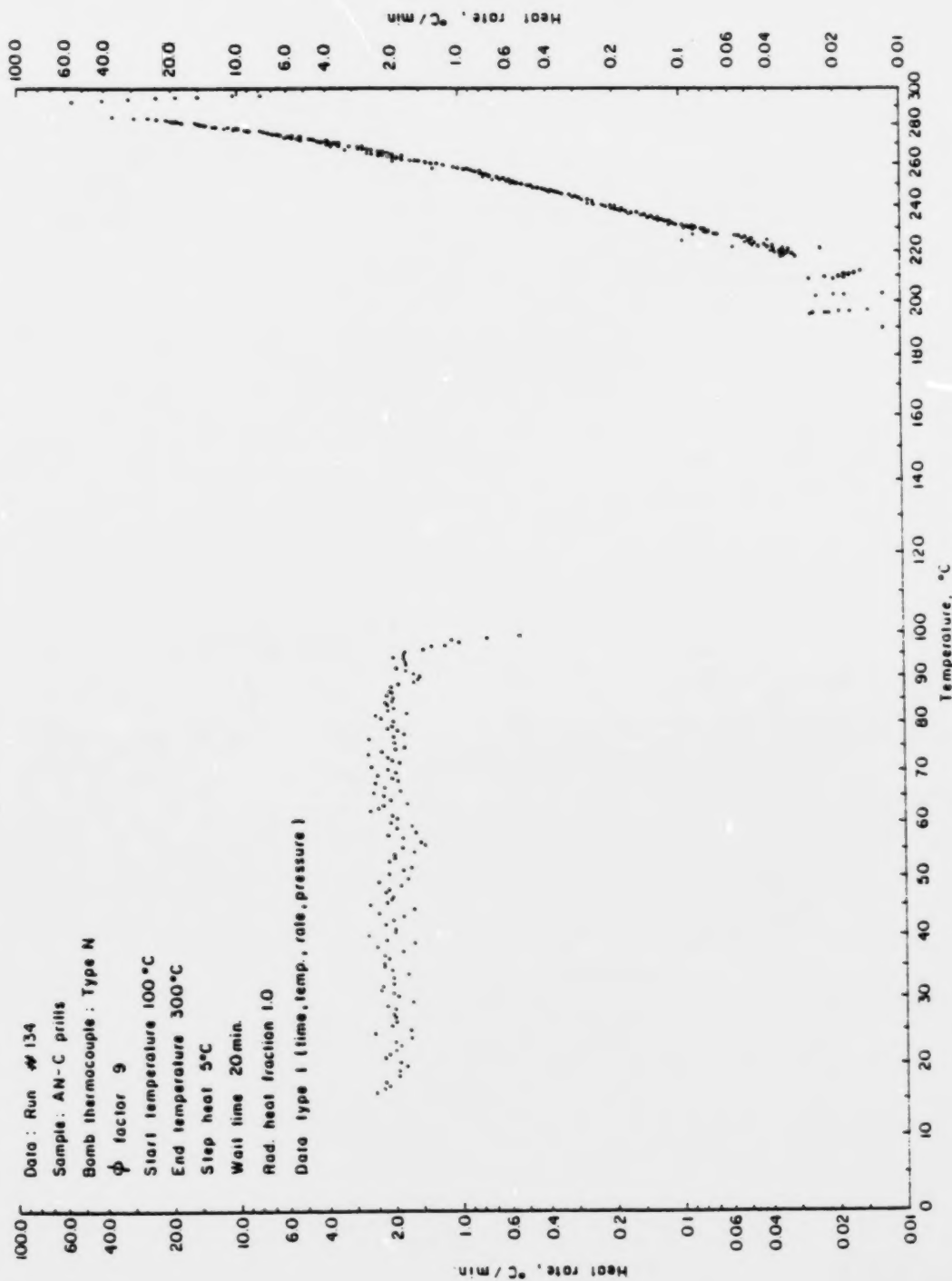


Fig. 2 - Self-heat rate vs temperature plot for AN decomposition.

HC cyl. bomb metal and teflon disc sealed
 Start temperature 100°C
 End temperature 350°C
 Step heat 5°C
 Sensitivity 0.02 °C/min
 Rad. heat fraction 1.0
 Wait time 20 min.
 $\phi = 9$

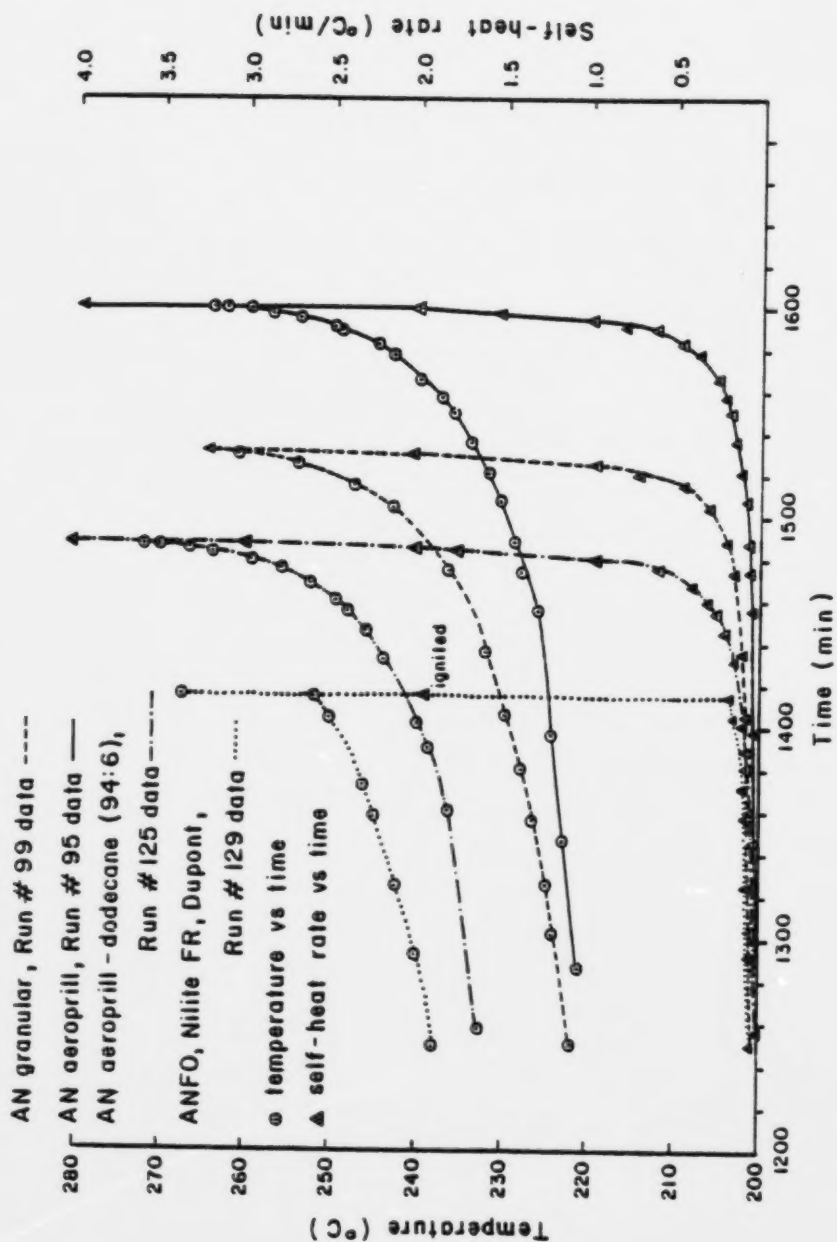


Fig. 3 - Temperature and self-heat rate vs time plots for AN and ANFO decomposition.

Table 4 - Data of isothermal age studies on AN and ANFO explosives

Run No.	Isothermal age		1st exotherm	Initial			Before ignition			ΔT_{AB} (°C)
	Temp (°C)	Time (min)	but stop (°C)	T_0 (°C)	M_0 (°C/min)	t_0 (min)	T (°C)	M (°C/min)	$t_0 + t$ (min)	
<u>AN granular</u>										
100	175	600	206.06	212.97	0.027	931.17	265.55	2.000	550.72	74.72
101	185	600	-	216.15	0.029	328.47	257.76	2.210	428.23	66.32
102	195	600	-	215.96	0.019	766.52	260.04	2.105	683.58	66.91
105	200	600	201.81	215.58	0.020	710.39	260.58	2.000	508.53	74.14
104	205	600	-	206.89	0.049	42.09	261.47	2.047	977.32	95.79
106	195	3000	-	216.39	0.035	3192.45	254.50	2.000	251.78	68.98
107	200	3000	201.87	206.03	0.023	2417.29	243.17	2.150	267.03	62.69
<u>AN aeroprills</u>										
109	195	3000	-	216.28	0.028	3198.74	251.48	2.066	210.61	65.32
108	200	3000	201.82	215.13	0.021	1121.19	249.32	2.064	288.99	67.90
112	195	6000	-	201.08	0.018	6069.03	242.23	2.166	371.10	62.51
<u>AN aeroprill - dodecane (94:6)</u>										
119	195	600	196.97	216.25	0.020	738.23	255.93	2.133	434.27	-
122	200	600	-	203.30	0.084	37.06	276.98	2.047	545.12	104.41
123	200	600	-	202.53	0.074	28.09	-	-	-	-
121	205	600	207.08	223.51	0.035	678.32	260.04	2.000	262.92	71.37
120	195	3000	-	236.59	0.059	3285.01	265.15	2.105	136.79	61.25
<u>AN-C prills, C.I.L.</u>										
136	190	600	-	216.31	0.032	786.96	266.34	2.100	420.07	75.95
137	195	600	-	226.44	0.040	822.30	260.63	1.935	248.42	58.69
138	200	600	-	201.53	0.041	34.84	267.21	1.906	725.52	91.84
<u>ANFO, AMEX II, C.I.L.</u>										
140	175	600	-	177.85	0.080	27.50	233.54	2.582	576.69	-
139	185	600	-	188.97	0.099	36.06	237.13	0.659	319.25	-
141	185	600	187.20	-	-	-	Ignited during step heat			-
<u>ANFO, Nitite FR, DuPont</u>										
143	175	600	-	191.26	0.031	725.87	234.43	1.000	269.55	75.96
142	185	600	-	187.82	0.110	25.32	244.54	0.176	1853.01	-

AN granular samples were isothermally aged at 175°C, 185°C, 195°C, 200°C and 205°C for 600 min, and at 195°C and 200°C for 3000 min. The AN granular samples were stable for more than 3000 min at 195°C. At the 200°C isothermal test, the temperature increased slowly for a period of about 2400 min before the exotherm was detected. There was no steady isothermal age at 205°C.

AN aeroprills were aged at 195°C and 200°C isothermally. It demonstrated that the sample was stable at 195°C even for 6000 min but it was unstable at 200°C. When the AN aeroprills-dodecane mixture was isothermally aged, it was stable at 195°C for 3000 min. The isothermal age tests at 200°C and 205°C were unstable and the results were not very consistent. After the AN aeroprills-dodecane mixture was heated to 200°C and cooled, it was observed that the oil layer was charred and floated on the top of the molten AN. It could be explained that the burning oil and molten AN were immiscible and due to the difference in densities between the two fluids, it was expected that the hydrocarbon would float on the surface. A few tests on AN-C prills also indicated that it was stable at the isothermal age temperature of 195°C for 600 min.

Commercial ANFO was a mixture of ammonium nitrate prills and fuel oil (94:6) with dye additive. From the previous step heat thermal stability tests, it was found that ANFO showed a different behaviour from AN prills. It was more reactive and the ignition was very vigorous. When the ANFO was heated to 175°C and cooled, it was observed that the oil was charred and some was condensed on the Teflon disk. AMEX II was not stable in the 175°C isothermal age test. At ignition, the temperature rate increased from 2.5°C/min to 192°C/min in 0.02 min. Another 185°C isothermal aging was performed on AMEX II. It instantly ignited at 237°C with a temperature rise of 8°C. Nilite FR from DuPont also showed instability at 175°C isothermal age test with fast ignition above 230°C. No consistent pattern in the self-heat curve was obtained for the isothermal age studies of ANFO. The data also indicated subsequent ignitions after the major one in some of the runs. The non-reproducibility of ANFO upon heating may be due to the wide range of values for the flash point of fuel oil (18). However, the reaction mechanism of this complex material was not identified.

C. Comparison of sample thermocouple and bomb thermocouple in temperature measurement

Since the bomb thermocouple (Nisil/Microsil, type N) is attached on the outside of the sample bomb, the temperature response of the measurement system is dependent on how quickly the sample and bomb together respond to a change in temperature. The speed with which the sample/bomb system responds is dependent on the mass of the bomb, the specific heat of the bomb, the sample contact area in the bomb and the interfacial heat transfer coefficient for the materials of interest.

In order to investigate the measurement problem at high self-heat rates, some experiments were performed by using a type N thermocouple insulated with silicone fluid and glass capillary tube as a sample thermocouple. It was placed directly in contact with the sample and positioned by the Teflon disk. The sample thermocouple was connected to the microprocessor which produced an output ΔT_{A-B} (sample-to-bomb temperature difference). Figure 4 illustrates the difference between the sample and bomb thermocouple in temperature measurements. The sample temperature and bomb temperature were more consistent for the self-heat rate below $5^{\circ}\text{C}/\text{min}$. At the lower self-heat rates, the heat transfer from the sample and bomb was adequate so that the bomb heat rate was close to the sample heat rate. However, at high heat rates, the heat transfer reached a limiting value while causing the sample temperature to actually run away from the bomb. The sample temperatures were lower than the bomb temperatures by a fraction of a degree as shown in Fig. 4. This could be due to the difference in insulation and their response time. The sample and bomb thermocouples were checked and it was found that the response was fast enough to track the temperature change.

The set up for this study was not very suitable for the AN sample because it decomposed after melting. The molten material splashed to the calorimeter and caused corrosion, ground fault and bomb temperature measurement problems.

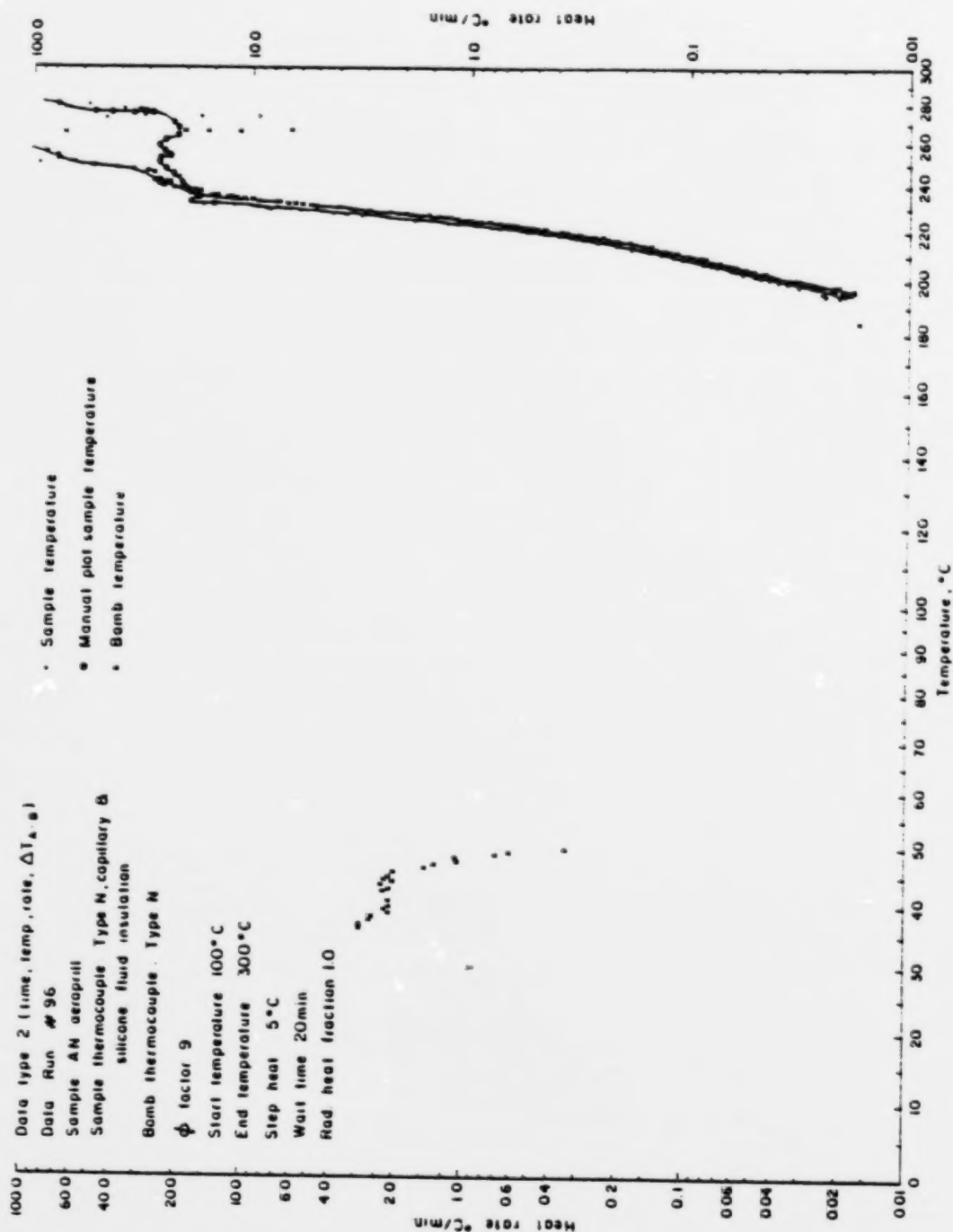


Fig. 4 - Comparison of sample thermocouple and bomb thermocouple in temperature measurement.

III. Modification of Existing ARC System

A. Calorimeter ground fault tracer

In the present ARC system, the power management module (PMM) provides power to the jacket heater elements and the radiant heater upon digital command from the microprocessor unit. A built in ground fault detection circuitry is included to provide protection against shorting of heater elements to the jacket. However, when a ground fault occurs, it is impossible to identify which of the nine heaters is causing the fault.

In our laboratory, a switching box was built and placed between the calorimeter and the PMM. Whenever the ground fault occurred, the problem causing heater could be identified by disconnecting the heaters individually during the trouble shooting process. The circuit diagram is shown in Fig. 5.

B. Modification of pressure transducer connection

In the original assembly of pressure measurement, the spherical bomb is directly hooked up to the fixed bomb adaptor in the calorimeter top, then to the pressure transducer. When the corrosive material splashes on the outlet, it will cause cleaning problems and damage.

In order to eliminate the problems in pressure measurement, a connection was designed to hook up a bomb to a 0.159 cm (1/16") S.S. tubing which connects to a pressure transducer. The transducer was also modified to reduce the dead volume and the 1/16" S.S. tubing could be replaced easily. Figure 6 is the drawing of the modified connection of the system. This set up facilitates the study of the pressure effect in the thermal decomposition of explosives.

C. Enlargement of the neck size of a spherical bomb

Due to the solid size of the explosive samples, loading difficulties exist. A spherical bomb with 0.138 cm (1/8") O.D. neck is converted to a 0.476 cm (3/16") O.D. tube. This conversion probably could solve the loading problem in future experiments.

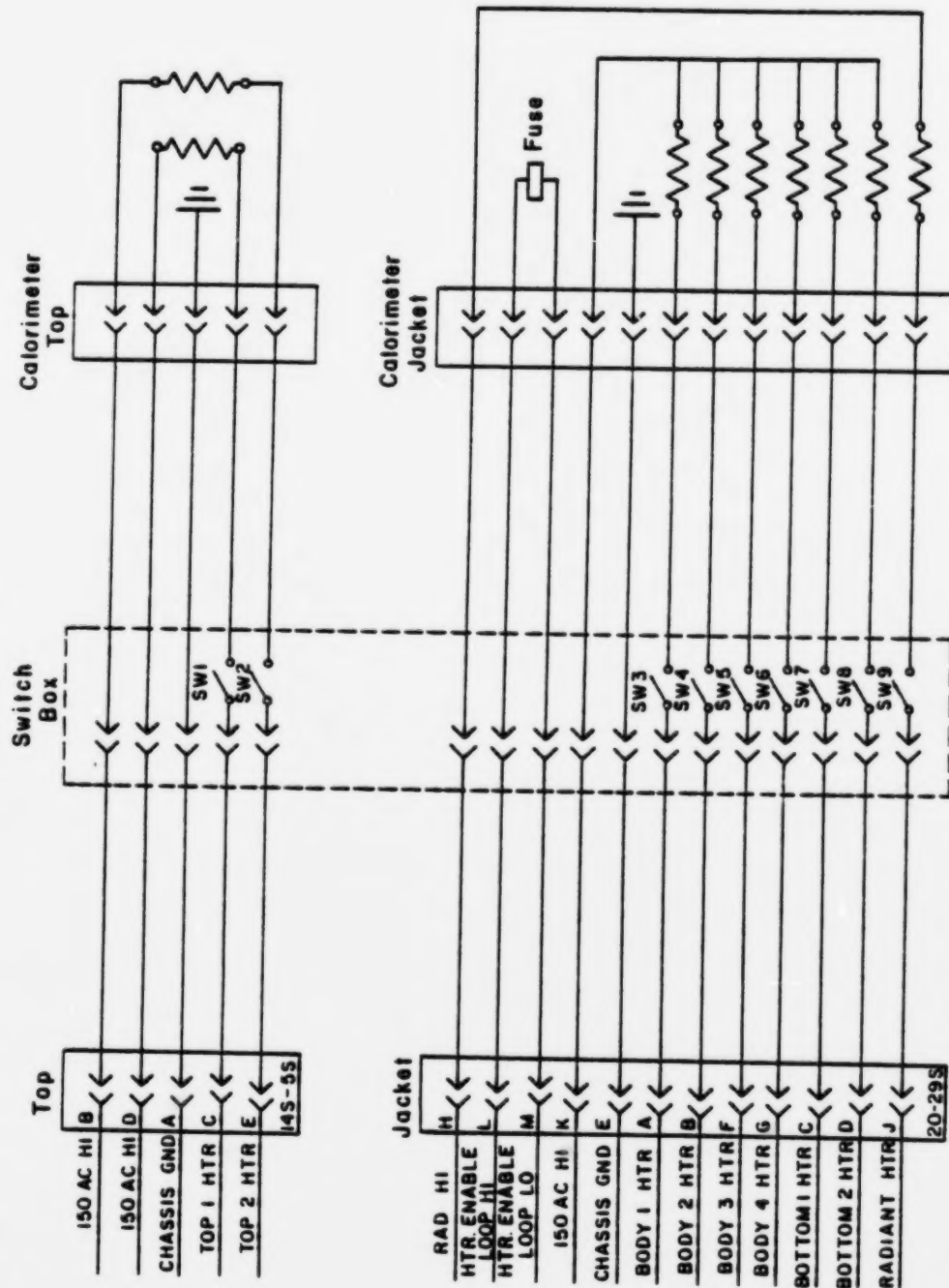


Fig. 5 - ARC ground fault tracer.

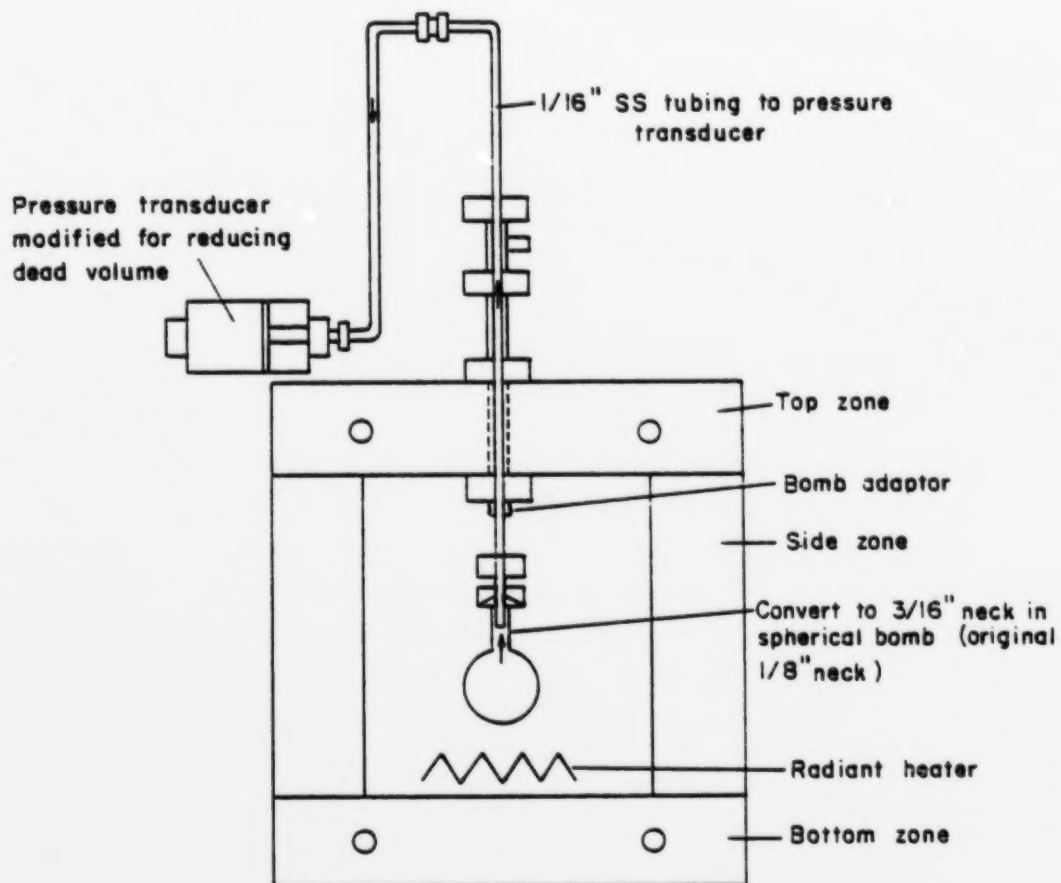


Fig. 6 - Modified spherical bomb and connection to the pressure transducer.

CONCLUSION

Step heat method was available to study the phase transitions but it could only detect the temperature range at which the transitions took place. It was found that the endothermic phase transitions were more reproducible at 124°C to 126°C and at the melting point. The AN aeroprills did not show the endothermic transition at 40°C as AN granular sample. The melting point shifted to lower temperature when 1% water was added to AN aeroprills. It indicated the phase changes could be shifted to lower or higher temperature by the presence of moisture or various compounds.

Thermal stability step heat test of AN prills and ANFO indicated the decomposition started in the range of 190°C to 210°C and the major exotherm leading to ignition occurred above 210°C. The temperature before ignition ranged from 240°C to 260°C. The commercial ANFO showed different characteristics at ignition which were fast, vigorous but non-reproducible.

Isothermal age studies indicated the AN granular, AN prills and AN prills - dodecane mixture survived the isothermal period for 600 min at 195°C but they started to decompose above 200°C. The commercial ANFO contained complex ingredients with more reactive properties and no consistent pattern of self-heat curve was found. The exotherms were detected as early as 175°C.

The kinetic data is not extracted in this test since it is not a simple decomposition. In order to predict the thermal hazards of high-energy materials, it is necessary to identify the component reactions of complex decomposition processes that are responsible for self heating to explosion. The kinetic constants must be measured for those specific component reactions. It is erroneous and dangerous to base hazards prediction on a single set of kinetic constants.

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